Tetrahedron Letters No. 30, pp. 2821-2824, 1971. Pergamon Press. Printed in Great Britain.

NMR STUDIES OF ORGANOMERCURY REDISTRIBUTION REACTIONS

F.G. Thorpe, T.N. Huckerby, P.H. Lindsay, S.W. Breuer.

(Chemistry Department, University of Lancaster, Lancashire)

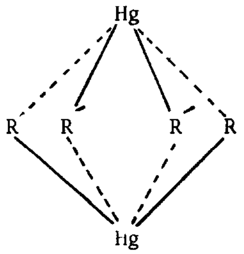
(Received in UK 7 June 1971; accepted in UK for publication 24 June 1971)

As part of a series of investigations concerning the exchange reactions and spectroscopic properties of organometallic compounds, we have examined the reaction between symmetrical organomercury compounds usually represented by equation (I)

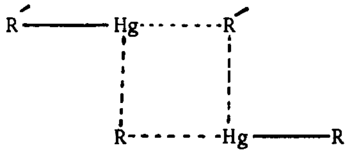
$$R_2Hg + R'_2Hg^* \rightleftharpoons R'_2Hg + R_2Hg^* \qquad (I)$$

Radioactive mercury can be used as a label to demonstrate that reaction occurs.

Although other redistribution reactions of organomercury compounds have been examined in detail, and established as electrophilic substitutions, (1) the mechanism of the above process (I) has remained in doubt. Isotopic exchanges of this type have been observed for a number of compounds (mostly aryl derivatives), and it has been reported (2) that unsymmetrically disubstituted mercurials are not formed during the reaction. Since there are many reports of the preparation of similarly constituted unsymmetrical organomercurials (3) it was concluded that the exchange takes place by way of a six-centre transition state (I) (2,4) in which the two metal atoms become equivalent. A four-centre transition state (II) would require the formation of the unsymmetrical species as an intermediate.



(I)



(II)

Detection of unsymmetrical intermediates in the products from exchange reactions has been reported only under more extreme conditions. For example, dibenzylmercury and diphenylmercury are reported to give upon fusion together $C_6H_5.CH_2HgC_6H_5$ as well as other reaction products.(5)

In experiments designed to detect the presence of unsymmetrical compounds under mild conditions in solution we have examined the p.m.r. spectra of solutions of pairs of symmetrical mercurials which had been shown to undergo radioisotopic exchange. Di-(acetaldehyde)mercury, Hg $(CH_2.CHO)_2$, was commonly used as one of the reactants because the methylene proton signals were found to be convenient structural indicators. For the systems studied, the p.m.r. spectra showed that a third organomercury compound appeared in solution shortly after mixing. This is illustrated in Figure 1 for the reaction between $Hg(C_6H_5)_2$ and $Hg(CH_2.CHO)_2$. For di-(acetaldehyde)mercury alone, the methylene region of the spectrum consists of symmetrically disposed satellite doublet signals on each side of the main methylene doublet; their separations give the value of the $^2J(^{199}HgCH)$ coupling constant (197 Hz).

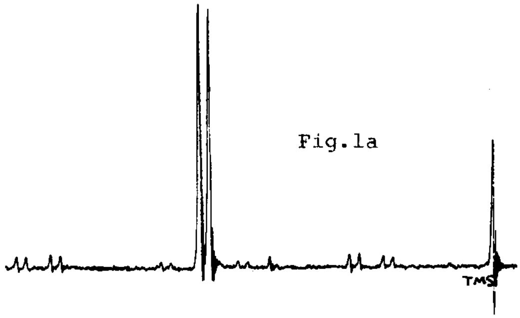


Fig.1a

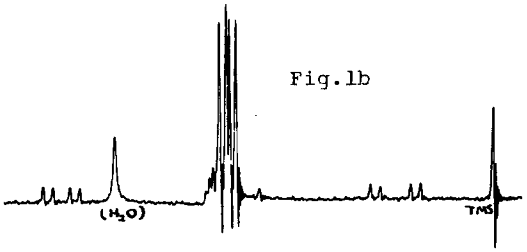


Fig.1b

Figures 1a and 1b show the methylene region for this compound when mixed with diphenylmercury when pyridine (1a) and DMSO-d_6 (1b) were used as solvents. In both these solvents additional satellite signals appear on mixing; in DMSO a second central methylene signal is also observed. These spectral changes indicate the presence in solution of a new species, $C_6H_5HgCH_2CHO$. In pyridine the methylene of this new species has the same chemical shift as in di-(acetaldehyde)mercury, but the value of $^2J(HgCH)$ is reduced+.

+ The changes in the values of $^2J(HgCH)$ are consistent with the general observation that the coupling constant increases as the groups attached to mercury become more strongly electron withdrawing.

In DMSO the new species can be more readily identified because its methylene signal is displaced to a chemical shift of $\delta=2.41$p.p.m., while the corresponding signal for $Hg(CH_2CHO)_2$ is at $\delta=2.37$ p.p.m. The spectral parameters for other exchange systems are summarised in the Table; unsymmetrical intermediates were observed for all these systems.

TABLE

NMR parameters for the methylene group of $R\text{-}Hg\text{-}CH_2CHO$ formed by reaction of R_2Hg & $Hg(CH_2CHO)_2$

	Pyridine solvent		DMSO solvent	
R-Group	^2J(HgCH)	$\Delta\delta$ (p.p.m.)	^2J(HgCH)	$\Delta\delta$ (p.p.m.)
Phenyl	158	0	161	0.04
p-methoxyphenyl	158	0	-	-
p-Dimethylaminophenyl	153	0	154	0.01

($\Delta\delta$ is the difference between the chemical shifts for the methylene group in $Hg\ (CH_2.CHO)_2$ and $R\text{-}Hg\text{-}CH_2.CHO$).

We conclude, therefore, that the transition state (1) does not accurately describe the mechanism of this process. The reaction certainly involves an unsymmetrical intermediate, and so should be represented as in equation (2).

$$R_2Hg + R'_2Hg^* \rightleftharpoons RHgR' + RHg^*R' \qquad (2)$$

The transition state is most probably a four-centre system (II).

In an attempt to obtain further evidence to support these conclusions, pairs of symmetrical mercurials were allowed to react in solution at room temperature, and the mass spectra of the mixtures examined. For most of the systems investigated the spectra indicated the presence of the unsymmetrical species. However, it was shown that these unsymmetrical compounds could be formed in the mass spectrometer, so this technique does not provide unambiguous evidence concerning the reactions in solution.

We wish to thank the S.R.C. for a Research Studentship (to PHL).

References

1. C.K. Ingold, <u>Helv.Chim.Acta</u> <u>47</u> 1192 (1964)
2. O.A. Reutov. J. Hun-geng, T.A. Smolina, <u>Izv.Akad.Nauk SSSR, Otd. Khim.Nauk 559 (1959)</u>
3. L.G. Makarova & A.N. Nesmeyanov "<u>The Organic Compounds of Mercury</u>", North-Holland, Amsterdam 1967, Chapter 12.
4. F.R. Jensen, B. Rickborn, "<u>Electrophilic Substitution of Organomercurials</u>", McGraw-Hill, 1968, p.186
5. M.D. Rausch, J.R. Van Wazer, <u>Inorganic Chem.</u> <u>3</u> 761 (1964)